

Recovery of Picloram and 2,4-Dichlorophenoxyacetic Acid from Aqueous Samples by Reversed-Phase Solid-Phase Extraction

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Extensive preparation of samples before chromatographic analysis is usually the most time-consuming process in the determination of many organic compounds in environmental matrices. In the past, removal of some organics from aqueous solution was commonly done by liquid/liquid extraction. However, the introduction of stable, covalently bonded reversed-phase sorbents now allows efficient removal of hydrophobic compounds from aqueous solution by adsorption on a chromatographic support. Solid-phase extraction is not a new technique. However, the procedure is more convenient today because of the commercial availability of ancillary equipment and prepackaged disposable adsorption cartridges in a variety of sorbents (1, 2).

Solid-phase extraction on bonded-phase organosilica based sorbents is an emerging technology for the analysis of chemicals of environmental significance. Environmental applications of solid-phase extraction for organic pollutant determinations in water have included the isolation of chlorophenolics (3, 4), azarenes (5), priority pollutants (6, 7), PAH and PCB's (8), and the trace enrichment of oil- or jet-fuel-contaminated water (9, 10).

Pesticide residue determinations in water by solid-phase extraction have been published for the insecticides lindane, heptachlor, aldrin, endosulfan, dieldrin, DDT, and zolone (11), aldicarb (12), and carbaryl (13, 14) and for the herbicides paraquat (15), paraquat and diquat (16), fluridone (17, 18), pyrazon (19), 2,4-D, 2,4,5-T, and silvex (20), atrazine, simazine, 2,4-D, silvex, and 2,4,5-T (21), and certain triazines (22). A solid-phase extraction method for the analysis of endrin, lindane, methoxychlor, and toxaphene has been submitted as an alternative test procedure to the current EPA (Environmental Protection Agency) approved method (23). If approved, the proposed technique would amend the National Primary Drinking Water Regulations to eliminate the liquid/liquid extraction step in the current USEPA test procedure for these four organochlorine pesticides, replacing it with a solid-phase extraction technique. Comprehensive reviews of analytical procedures for pesticide analysis from water have been published (24-26).

In the procedure presented herein, the herbicides picloram (4-amino-3,5,6-trichloropicolinic acid) and 2,4-dichlorophenoxyacetic acid (2,4-D) are recovered from aqueous samples via solid-phase extraction on reversed-phase sorbents as an alternative to liquid/liquid extraction. Previously, solid-phase extraction on reversed-phase sorbents was used to effect purification of picloram-containing samples that had first been concentrated by partitioning with diethyl ether (6, 7). Current modification of earlier methods accomplishes both sample purification and sample concentration.

While this report was in preparation, two solid-phase extraction methods for chlorophenoxy acid herbicides, including 2,4-D, were published by Hoke et al. (20) and Sherma (21). However, neither of these procedures included picloram and thereby did not address samples that could contain both picloram and 2,4-D.

In this report, differential elution from the bonded-phase sorbent is used to cleanly separate picloram and 2,4-D from

each other. Such a multistage process is not limited to herbicide analysis and should find application to any multiresidue samples sorbed on reversed-phase supports and differing sufficiently in hydrophobicity as do picloram and 2,4-D.

EXPERIMENTAL SECTION

Apparatus. The liquid chromatograph consisted of a Waters Model 6000A solvent pump equipped with a Model 720 system controller, Model 710B intelligent sample processor, automated solvent switching valve, a Model 440 UV absorbance detector, and a Laboratory Data Control SpectroMonitor III variable wavelength UV absorbance detector, a Houston Instrument strip-chart recorder, and a Perkin-Elmer Sigma 10B data handling system.

Reagents and Chemicals. Spectrophotometric grade acetonitrile (ACN) and methanol (MeOH) were purchased from Burdick and Jackson Laboratories, Inc., and spectrophotometric grade glacial acetic acid (HOAc) was purchased from J. T. Baker Chemical Co. Potassium permanganate (KMnO₄), ACS grade, was purchased from Fisher Scientific and sodium hydrogen sulfite (NaHSO₃), ACS grade, from Alfa Products. The analytical standards, picloram, 99.0% purity and 2,4-D, 99+ % purity, were obtained from Dow Chemical Co. and PolyScience Corp., respectively.

Liquid Chromatographic Conditions. An Ultrasphere ODS, 5 μ m, spherical porous particle column, 15 cm by 4.6 mm i.d., 2UE5354N, from Altex Scientific, Inc., was used in this study with a CO:PELL ODS, 30-38 μ m, 7 cm by 2.1 mm i.d. guard column from Whatman, Inc. The liquid chromatographic mobile phases were acetic acid (4%)/acetonitrile (95:5 v/v) monitored at 254 nm for picloram or acetic acid (4%)/acetonitrile (60:40 v/v) monitored at 280 nm for 2,4-D and were pumped at a flow rate of 1.5 mL/min. (Note: Never allow these phases to remain idle in the system.)

Equipment for Solid-Phase Extraction. C₁₈ disposable extraction columns, part no. 7020-3, solvent reservoirs, adaptors, and a vacuum manifold were purchased from J. T. Baker Chemical Co. Polyethylene frits, 20 μ m, 1 $\frac{1}{16}$ in. diameter, were purchased from Analytichem International and a low-form Filtrator was purchased from Fisher Scientific.

Sample Fortification. Fortified samples were prepared by dissolving pure picloram and 2,4-D standards into separate water solutions. Appropriate amounts of each of these stock solutions were added together to aqueous samples to produce desired concentrations or the solutions were further diluted to produce the test concentrations.

Determination. Aqueous samples were acidified to pH 2 with concentrated sulfuric acid. Two Baker C₁₈ columns, each containing about 500 mg of sorbent in a disposable polypropylene column, were connected via adaptors in tandem with each other and with a 75 mL capacity polypropylene sample reservoir. A 1 $\frac{1}{16}$ in. polyethylene frit was placed at the bottom of the solvent reservoir. The apparatus was fitted into a side-arm filtering flask. Five milliliters of ACN followed by 10 mL of 4% HOAc in water were added separately and pulled through the adsorbent with vacuum (530 mmHg) at a flow rate of 10-12 mL/min. Before the adsorbent could dry, the sample was passed through the column, followed by 2 mL of 4% HOAc. The frit was removed from the solvent reservoir. Picloram was eluted with 9.0 mL of 25% HOAc directly into a 10-mL volumetric flask contained in a Fisher Filtrator or Baker vacuum manifold. To this eluted fraction, 0.5 mL of saturated aqueous KMnO₄ was added, and the mixture was allowed to remain at room temperature for 5 min. A 5 M solution of NaHSO₃ was added dropwise to reduce excess permanganate. The sample was diluted to 10.0 mL with 25% HOAc. The 2,4-D still remaining on the adsorbent was serially

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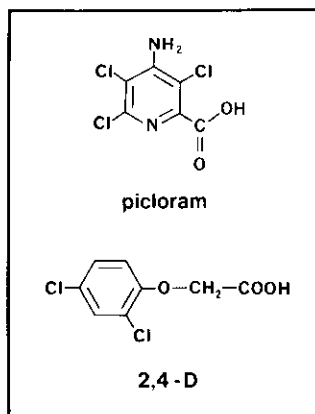


Figure 1. Chemical structures of the herbicides picloram and 2,4-D.

eluted with 4.5 mL of MeOH directly into a 5-mL volumetric flask contained in a Fisher Filtrator or Baker vacuum manifold. This fraction was diluted to 5.0 mL with MeOH. A 50- μ L aliquot of each fraction was injected into the chromatograph under the conditions appropriate for each as described above. External standard solutions were prepared by dissolving pure picloram and 2,4-D standards into separate methanol solutions. Appropriate dilutions of these stock solutions were prepared to obtain standards with a range of concentrations. These standards were randomly selected and injected as every fourth sample by the autosampler.

Caution: Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or other wildlife—if they are not handled or applied properly. Use all pesticides selectively and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers.

RESULTS AND DISCUSSION

Picloram and 2,4-D (Figure 1) are formulated together in some of the herbicidal preparations that bear the trade name Tordon. Concomitant analysis for the presence of trace residues of picloram and 2,4-D in environmental waters necessitates development of a rapid, reliable, and sensitive analytical protocol. Solid-phase extraction of these compounds on reversed-phase sorbents is an attractive alternative to more traditional methods that utilize liquid/liquid extraction for the removal of these herbicides from aqueous samples.

Picloram is a much polar compound than 2,4-D. Being less hydrophobic, its extraction from environmental water samples requires a greater amount of reversed-phase sorbent than that needed for 2,4-D. One column of 500 mg is insufficient to produce desirable recovery of picloram. A two-column tandem assembly is necessary to provide 1.0 g of sorbent (500 mg each) for sufficient recovery from 200-mL samples. A similar effect was noted by Rostad et al. (3) in their report of the recoveries of 27 phenols, PAH's, and sulfur, oxygen, and nitrogen heterocycles from 500 mg of cyclohexyl bonded phases. They too observed limited recovery for very water-soluble, very polar compounds. They minimized this problem by reducing the sample volume applied to the 500 mg cyclohexyl column. But reducing sample volume adversely affects the amount of substance detectable. For the analysis of picloram and 2,4-D, it was preferable to increase the amount of sorbent, to allow sufficient recovery from 200-mL samples.

The parameters of sample volume, sorbent mass, and solute hydrophobicity are interrelated. For methods development of environmental samples on reversed-phase sorbents, a 200-mL sample volume, 100 ppb sample concentration, and 1.0 g of sorbent are recommended starting values (1). The C_{18} sorbent used in this report is now available prepackaged in 1000 mg (1.0 g) quantities per cartridge, which can effectively replace the two-column tandem assembly with a single column.

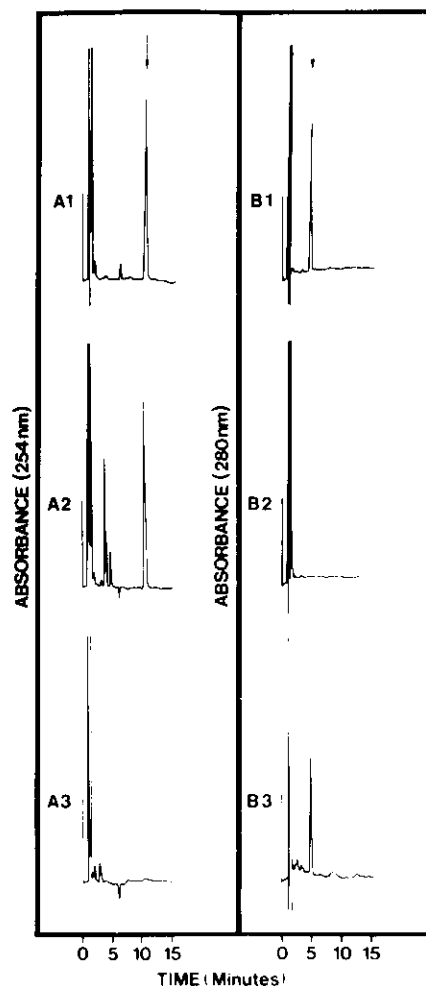


Figure 2. Chromatograms of picloram (A1) 44.2 ng and 2,4-D (B1) 46.5 ng standards; the first fraction desorbed by 25% acetic acid (A2 and B2); the second fraction desorbed by methanol (A3 and B3). The "A" chromatograms were obtained under conditions appropriate for the detection of picloram and the "B" chromatograms for 2,4-D.

Because picloram and 2,4-D differ sufficiently in hydrophobicity, selective desorption of the individual compounds from the extraction sorbent is possible. Variation in solvent elutropic strength is utilized in the technique presented here to accomplish preferential desorption of the solutes picloram and 2,4-D when simultaneously sorbed on an extraction column. Figure 2 illustrates the chromatographic results. The chromatograms A1 and B1 depict the elution of picloram and 2,4-D standards obtained under the conditions of isocratic mobile-phase composition and detector wavelength appropriate for each component. The four remaining chromatograms, A2, B2, A3, and B3, all stem from a single 200-mL distilled water sample that was spiked with 50 ppb each of picloram and 2,4-D. A2 and B2 are chromatograms of the same elution fraction (i.e., the first desorption with 25% acetic acid) injected under the proper conditions for detecting picloram (A2) or 2,4-D (B2). A3 and B3 are chromatograms of the second fraction eluted with methanol and chromatographed under conditions appropriate for picloram (A3) or 2,4-D (B3). The figure clearly shows that picloram and 2,4-D are cleanly separated in a serial elution by 25% acetic acid followed by methanol from the reversed-phase sorbent. No 2,4-D is detected (B2) in the picloram-containing fraction (25% HOAc) nor is picloram detected (A3) in the 2,4-D-containing fraction (MeOH).

Figure 3 illustrates results typical of natural stream water samples. The chromatograms C1 and D1 depict the elution of picloram and 2,4-D standards obtained under the conditions

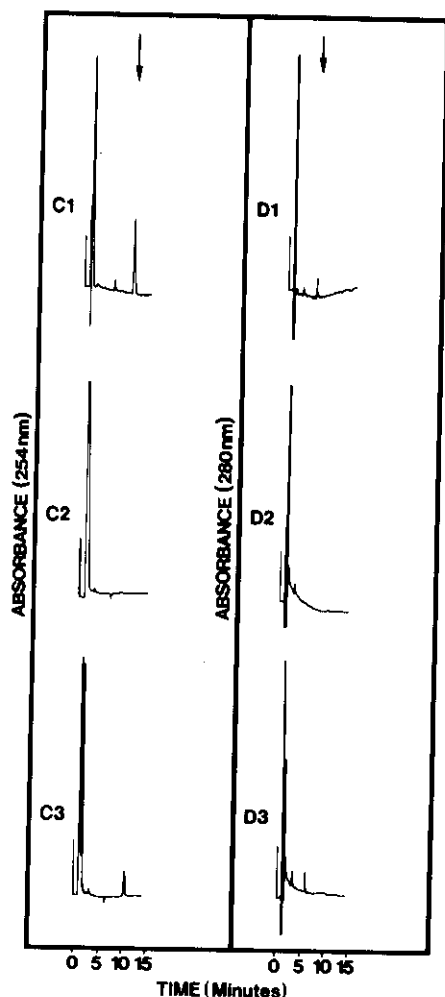


Figure 3. Chromatograms of picloram (C1) 67.5 ng and 2,4-D (D1) 22.9 ng standards; an unfortified natural water sample serially desorbed first by 25% acetic acid (C2) followed by methanol (D2); a fortified natural water sample serially desorbed first by 25% acetic acid (C3) followed by methanol (D3). The "C" chromatograms were obtained under conditions appropriate for the detection of picloram and the "D" chromatograms for 2,4-D.

of isocratic mobile-phase composition and detector wavelength appropriate for each component. The center chromatograms in Figure 3, C2 and D2, demonstrate the background absorbance from an unfortified natural water sample serially desorbed first by 25% acetic acid (C3) followed by methanol (D3). The lower pair of chromatograms in Figure 3, C3 and D3, portray the recovery of picloram and 2,4-D, respectively, from a 200-mL natural water sample that was fortified with 24.3 ppb of each of these two herbicides.

The two-stage desorption of aqueous samples (200 mL) simultaneously spiked with picloram and 2,4-D at four fortification levels (250, 50, 25, and 5 ppb) yielded an overall recovery level of 98.2% (3.9% standard deviation) for picloram and 91.9% (10.7% standard deviation) for 2,4-D (Table I). Single-stage desorption by the solvent of greater eluting strength (i.e., MeOH) produces equivalent recoveries of each solute into the same fraction. However, collecting picloram and 2,4-D into the same fraction from the reversed-phase solid-phase extraction column also includes coeluting contaminants that would have retention times longer than that of picloram and shorter than that of 2,4-D on the reversed-phase analytical column. The elution order of picloram and 2,4-D from a reversed-phase analytical column is analogous to the desorption order from a reversed-phase solid-phase extraction column. Therefore, complete separation of the two components is desirable because it improves the subsequent

Table I. Recovery of Variable Molar Amounts of Picloram and 2,4-D from Fortified Water Samples of Constant Volume (200 mL)

fortification, ppb	n	% average recovery	
		2,4-D	picloram
5.0	2	96	102
25.0	3	91.7	101.1
50.0	4	88.2	97.2
250.0	3	94.4	94.1
overall		91.9	98.2
SD		10.7	3.9

^a There is no statistical difference among the means for recovery of 2,4-D or picloram ($\alpha = 0.01$) by Tukey's Studentized range test (HSD).

analytical results.

Registry No. 2,4-D, 94-75-7; picloram, 1918-02-1; H₂O, 7732-18-5.

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Design and Evaluation of a Capillary Gas Chromatography-Atomic Absorption Spectrometer Interface

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Quartz tube atomizers have been frequently used in organometallic speciation studies (1-4). A variety of tube material (5, 6), heating methods (6, 7), and interfaces (4, 5, 8) have been reported, but few systematic studies to improve the quartz tube atomizer, particularly the gas chromatographic interface, have been done.

Tubal dimensions should minimize analyte dilution before reaching the optical pathway of the atomic absorption spectrophotometer, yet maximize residence time in the light pathway. Ebdon et al. (6) found that a long narrow tube configuration gave the best sensitivity. Several studies have shown that H_2 enhances sensitivity (1, 4, 9), likely by hydrogen radicals (formed by catalytic activity of the quartz surface (7)) mediating analyte atomization (4, 9).

A gas chromatograph (GC)-atomic absorption spectrometer (AAS) interface should (a) preserve and transport the analyte compounds to the atomization region of the furnace in a minimum gas volume and (b) introduce the furnace support gases; this allows the use of a simple quartz T-tube design.

The purpose of this study was to improve an existing interface design (4) to allow efficient coupling of a capillary column to the quartz T-tube atomizer.

EXPERIMENTAL SECTION

Apparatus. The analytical system was assembled with a Varian 3400 gas chromatograph (GC), a quartz furnace (assembled at Health and Welfare Canada), an Instrumentation Laboratory Model 751 atomic absorption spectrometer (AAS), and a recording integrator (Varian Model 4270).

The GC was equipped with a split/splitless injector and a 15 m \times 0.32 mm DB-5 fused silica column (J&W Scientific, Inc.). Operating conditions were as follows: carrier gas, helium, 1.5 mL min^{-1} ; injector temperature, 200 $^{\circ}C$, splitless mode, 1 min post-injection solvent vent at 30 mL min^{-1} , temperature program isothermal at 50 $^{\circ}C$ for 1 min followed by linear ramping at 10 $^{\circ}C$ min^{-1} to 175 $^{\circ}C$ (held for 0.5 min).

About 60 cm of the fused silica column was extended from the GC oven to the AAS through an insulated, heated $1/4$ in. (0.64 cm) o.d. copper transfer tube. The transfer tube temperature (200 $^{\circ}C$) was maintained by a heating tape (Cole Palmer Co.), which was controlled by a time proportional temperature controller (Model 6100, Omega Engineering, Inc.). The temperature was monitored by a digital temperature indicator (Model 115, Omega Engineering, Inc.).

The atomic absorption spectrometer was equipped with a Pb hollow cathode lamp (IL Visimax). Operating conditions were as follows: hollow cathode lamp current, 3 mA; wavelength, 283.3 nm; band-pass, 0.5 nm; photomultiplier tube voltage, 700 V; single beam mode.

The quartz furnaces (Figure 1 and Figure 1 of ref 4) consisted of a quartz T-tube (upper tube 10 cm \times 9 mm o.d., 7 mm i.d.; lower tube 4 cm \times 6.25 mm o.d., 4 mm i.d.) heated electrically with 3.1 m of 25 gauge Chromel 875 resistance wire (Hoskins Alloys of Canada) coiled around the upper tube (furnace A, Figure 1, ref 4) or with 6.7 m of 26 gauge Chromel 875 wire coiled and embedded into the two refractory brick sections (furnace B, Figure

1) with refractory cement (Alundum cement, Fisher Sci. Co.). A layer of Fiberfrax ceramic fiber (The Carborundum Co.) insulated the quartz tube in furnace A, whereas none was used in furnace B. Insulation was removed around the inlet region of furnace A for air circulation. In furnace B, the insulation and heating elements were extended to the edge of the detector casing. The four Swagelok $1/8$ in. (0.32 cm) NPT to $1/8$ in. (0.32 cm) tube connections were mounted in the furnace casing (11 cm \times 4.8 cm o.d., 4 cm i.d.) as ports for electrical connections to the heating elements and to position two type K (chromel-alumel) thermocouples. Ceramic tubing (Omega Engineering, Inc.) mounted within the Swagelok connectors was used as electrical insulation. The furnace casing was held together with an aluminum mounting bracket. The furnace was positioned within the optical path of the AAS by an adjustable ball joint affixed to the mounting bracket.

Furnace temperature was controlled by a Model 6100 proportional temperature controller (Omega Engineering, Inc.) and monitored by a digital temperature indicator (Model 115, Omega Engineering, Inc.).

The interface between the capillary column and the quartz furnace utilized readily available parts (Figure 2, ref 4). A $1/4$ in. (0.64 cm) to $1/8$ in. (0.32 cm) Swagelok reducing union, modified with an attached $1/16$ in. (0.16 cm) stainless steel tubing gas inlet (E, Figure 2, ref 4), positioned either a section of ceramic tubing (8 cm \times $1/8$ in. (0.32 cm) o.d., $1/16$ in. (0.16 cm) i.d.) or quartz tube lined ceramic insert within the lower tube of the quartz furnace. A $1/8$ in. (0.32 cm) to $1/16$ in. (0.16 cm) Swagelok reducing union similarly modified with an attached $1/16$ in. (0.16 cm) stainless steel tubing gas inlet (J, Figure 2, ref 4) was mounted to the ceramic tube/insert as a gas tight connection for the capillary column. The quartz tube lined ceramic inserts were constructed from 0.53 mm deactivated fused silica (J&W Scientific, Inc.) centered within the ceramic tube with refractory cement (Alundum cement, Fisher Scientific Co.) and the interspace was sealed with sodium silicate.

Three interfaces were examined. Interface I used the ceramic tube. The end of the GC column was positioned 5 mm in front of the ceramic tube, at the T-tube junction.

Interface II used a ceramic insert which was 8 cm long (ceramic tube) with the fused silica extending out 5 mm from both ends. The tip of the insert was positioned at the T-tube junction. The GC column was backed up 6-7 mm from the tip, just outside the insulated region of the furnace.

Interface III used a ceramic insert which was 6.5 cm long (ceramic tube) with the fused silica extending out 17 mm at the end inserted into the furnace with 5 mm of fused silica at the other end. The 5-mm extension of fused silica at the GC column end of the insert simplified insertion of the 0.32-mm fused silica column through the insert. The air inlet (G, Figure 2, ref 4) was sealed and the air introduced by routing both the H_2 and air through a tee union into the H_2 #1 inlet. The insert tip was positioned at the T-tube junction. The end of the GC column was positioned 18-19 mm from the tip, just outside the insulated (and heated) region of furnace type B.

A timed furnace gas purge cycle was controlled by the GC electronics (Figure 2). The H_2 flow (45 mL min^{-1}) to H_2 #1 inlet of the GC-AAS interface was vented to a fume hood for the initial